Name ___________________________________Chem 161, Section: _______**Group Number:** ______

ALE 17. Redox Reactions: Oxidation-Reduction Reactions

(Reference: Sections 4.5 and 4.6 in *Silberberg 5th edition*)

When will hydrochloric acid not be enough to dissolve a metal?

The Model: Assigning Oxidation Numbers

Oxidation Number (O.N.): The charge or apparent charge that an atom in a *molecular* compound or ion would have if all of the electrons in its bonds belonged entirely to the more electronegative atom—i.e. the atom that more strongly attracts the shared electrons.

<u>Guidelines to Assign Oxidation Numbers</u>

1) In free elements (*i.e.*, in the uncombined state), each atom has an oxidation number of zero—e.g. Na, Zn, N_2, S_8, P_4, F_2
2) The oxidation number of monatomic ions is equal to the charge on the ion—e.g. the O.N. of Na^+ is +1, the O.N. of Cl^- ion is -1, that of Mg^{2+} is +2.
4) The oxidation number of fluorine in all of its compounds is -1.
5) The oxidation number of oxygen in most compounds (called "oxides") is -2—e.g. Na_2O, ZnO, SO_2, SO_3. In peroxides (e.g. Na_2O_2, H_2O_2) the oxidation number of oxygen is -1. In superoxides (O_2^{1-}), the oxidation number of oxygen is $-{}^1/_2$.
6) The oxidation number of hydrogen is +1, except when it is bonded to metals in binary compounds called hydrides in which its oxidation number is -1—e.g. NaH, CaH_2, AlH_3.
6) The sum of the oxidation numbers in a neutral compound is zero: H_2O: $2(+1) + (-2) = 0$
7) The sum of the oxidation numbers in a polyatomic ion is equal to the charge on the ion. The oxidation number of the sulfur atom in the SO_4^{2-} ion must be +6, for example, because the sum of the oxidation numbers of the atoms in this ion must equal -2: SO_4^{2-}: $(+6) + 4(-2) = -2$

Exercise

A. There are numerous compounds and polyatomic ions containing nitrogen and oxygen. None of these are peroxides or superoxides. Complete the following table.

Species	Oxidation number of each oxygen	Total charge of all oxygen atoms	Total charge of all nitrogen atoms	Average oxidation number of each nitrogen atom
NO				
NO_2				
N_2O				
NO_2^-				
NO_3^-				

The Model: Oxidizing and Reducing Agents

Many metals dissolve in hydrochloric acid. Copper does not. To dissolve copper, one must use an oxidizing acid, such as nitric acid. The net ionic equation for that process is:

$$\mathbf{3\ Cu(\mathit{s})\ +\ 2\ NO_3^-(\mathit{aq})\ +\ 8\ H^+(\mathit{aq})\ \rightarrow\ 3\ Cu^{2+}(\mathit{aq})\ +\ 2\ NO(\mathit{g})\ +\ 4\ H_2O(\mathit{l})} \qquad (\mathbf{1})$$

The reaction may be separated into ***half-reactions***:

Reduction: $[\ NO_3^-(aq)\ +\ 4\ H^+(aq)\ +\ 3\ e^-\ \rightarrow\ NO(g)\ +\ 2\ H_2O(l)\ ] \times 2$ (**2**)

Oxidation: $[\ Cu(s)\ \rightarrow\ Cu^{2+}(aq)\ +\ 2\ e^-\ ] \times 3$ (**3**)

In the above reaction, nitrate (from nitric acid) is acting as the ***oxidizing agent*** (*i.e.*, the "agent of oxidation") and copper metal is (reciprocally) the ***reducing agent*** (*i.e.*, the "agent of reduction").

Key Questions

1. Assign oxidation numbers to all atoms in the reaction between copper and nitric acid. Write the oxidation numbers *above* each atom in **equation 1**, above.

2. Compare the amounts by which the oxidation states of Cu and N change and the numbers of electrons involved in the half-reactions (equations **2** and **3**). Briefly detail your findings—i.e. Justify why you answered the way you did..

3. In the reaction between copper and nitric acid (**eqn 1**), copper is *oxidized.* What does it mean (in terms of its oxidation state) for a species to be oxidized? to be reduced?

4a. An element within the oxidizing agent is being oxidized / reduced, and within the reducing agent an element is being oxidized / reduced. (Circle your responses.)

b. Explain how your answer to Question 4a makes sense in terms of losing / gaining electrons.

5a. Why is the reduction half-reaction (eqn **2**) multiplied by 2 and at the same time the oxidation half-reaction (eqn **3**) multiplied by 3?

b. Why can't the net ionic equation between copper and nitric acid simply be as follows? (*Hint*: While the number of each atom may be balanced, there is something that isn't.)

$$\mathbf{Cu(\mathit{s}) + NO_3^-(\mathit{aq}) + 4\,H^+(\mathit{aq}) \rightarrow Cu^{2+}(\mathit{aq}) + NO(\mathit{g}) + 2\,H_2O(\mathit{l})}$$

6. <u>True</u> or <u>False</u>: An oxidation reaction *must* occur when a reduction reaction takes place.

Justify why you answered the way you did.

Exercise

B. One type of breathalyzer employs the following net ionic reaction:

$$\mathbf{2\,Cr_2O_7^{2-} + 3\,C_2H_5OH + 16\,H^+ \rightarrow 4\,Cr^{3+} + 3\,HC_2H_3O_2 + 11\,H_2O(\mathit{l})}$$

Ethyl alcohol (C_2H_5OH, present in a drinker's breath) dissolves in the aqueous solution and is oxidized to acetic acid, $HC_2H_3O_2$. The amount of alcohol present in one's breath determines the amount of dichromate ion ($Cr_2O_7^{2-}$) that is consumed. Dichromate is brightly colored (orange), so the decrease in color of the solution indicates how much alcohol one has recently consumed.

① In the reaction above, assign (average) oxidation numbers to chromium atoms and to carbon atoms on the reactant and product sides of the above reaction.

② Of dichromate and ethyl alcohol, which species is the oxidizing agent and which is the reducing agent? Justify why you answered the way you did.

③ Balance the following half-reactions (by adding coefficients to the water molecules, hydrogen cations, and electrons).

$$\mathbf{\_\_\_\ Cr_2O_7^{2-} + \_\_\_\ H^+ + \_\_\_\ e^- \rightarrow \_\_\_\ Cr^{3+} + \_\_\_\ H_2O(\mathit{l})}$$

$$\mathbf{\_\_\_\ C_2H_5OH + \_\_\_\ H_2O(\mathit{l}) \rightarrow \_\_\_\ HC_2H_3O_2 + \_\_\_\ H^+ + \_\_\_\ e^-}$$

The Model: Relative Reactivities of Metals and Single Displacement Reactions

Consider taking the elemental form of one metal (A) and placing it in an aqueous solution of the cations of a second metal (B). If there is a reaction, it would be evidenced by the discoloration of either the surface of the piece of metal A or the solution or both. If the reaction occurs, then A is more reactive than B. If no reaction takes place between metallic A and an aqueous solution of B^{b+}, then B is more reactive than A.

Suppose we have the following metals and corresponding aqueous solutions: aluminum and $Al(NO_3)_3(aq)$; lead and $Pb(NO_3)_2(aq)$; nickel and $Ni(NO_3)_2(aq)$; and silver and $AgNO_3(aq)$. Further suppose we place each metal in aqueous solutions of the cations of the *other* metals. We would observe the following net ionic ***single displacement reactions*** (or non-reactions):

$2\,Al(s) + 3\,Pb^{2+}(aq) \rightarrow 2\,Al^{3+}(aq) + 3\,Pb(s)$
$2\,Al(s) + 3\,Ni^{2+}(aq) \rightarrow 2\,Al^{3+}(aq) + 3\,Ni(s)$
$Al(s) + 3\,Ag^{+}(aq) \rightarrow Al^{3+}(aq) + 3\,Ag(s)$

$Ni(s) + Al^{3+}(aq) \rightarrow$ N.R.
$Ni(s) + Pb^{2+}(aq) \rightarrow Ni^{2+}(aq) + Pb(s)$
$Ni(s) + 2\,Ag^{+}(aq) \rightarrow Ni^{2+}(aq) + 2\,Ag(s)$

$Pb(s) + Al^{3+}(aq) \rightarrow$ N.R.
$Pb(s) + Ni^{2+}(aq) \rightarrow$ N.R.
$Pb(s) + 2\,Ag^{+}(aq) \rightarrow Pb^{2+}(aq) + 2\,Ag(s)$

$Ag(s) + Al^{3+}(aq) \rightarrow$ N.R.
$Ag(s) + Pb^{2+}(aq) \rightarrow$ N.R.
$Ag(s) + Ni^{2+}(aq) \rightarrow$ N.R.

Key Questions

7. Using the model, above, rank aluminum (Al), lead (Pb), nickel (Ni), and silver (Ag) from most reactive to least reactive.

   Most reactive → Least Reactive

   _____ > _____ > _____ > _____ >

8. Refer to the Activity Series for Metals in your textbook. Find Al, Pb, Ni, and Ag on the Activity Series. How does the position of a metal relate to its chemical reactivity?

9. If a strip of zinc metal is added to an aqueous solution of copper(II) sulfate, over time one will notice that a brown precipitate accumulates on the strip of metal and that the solution becomes progressively less blue in color. Use the Activity Series to explain what chemical reaction is occurring. As part of your explanation, write the balanced net ionic equation that occurs between zinc and copper(II).

10. Hydrogen is often written on the Periodic Table on Group IA (Column 1), because the chemical reactivity of hydrogen cations often resembles that of the cations of the alkali metals. In the elemental form, however, hydrogen exists as a diatomic gas. Use the Activity Series for Metals in your textbook to explain the following.

a. Explain why the following reaction occurs when calcium is added to water:

$$\mathbf{Ca(\mathit{s}) + H_2O(\mathit{l}) \rightarrow CaO(\mathit{aq}) + H_2(\mathit{aq})}$$

(The calcium oxide then decomposes in water to yield additional hydrogen gas and becomes calcium hydroxide.)

b. Explain why zinc metal dissolves in hydrochloric acid according to:

$$\mathbf{Zn(\mathit{s}) + 2\ HCl(\mathit{aq}) \rightarrow ZnCl_2(\mathit{aq}) + H_2(\mathit{g})}$$

c. Explain why copper metal does not dissolve in hydrochloric acid.